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Nouvelles réactions mettant en jeu des réactifs de Grignard et des complexes du nickel. Formation d'oléfines à partir d'alcools allyliques.

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Substitution at Phosphorus in the Reaction Between Dichlorobis(triphenylphosphine)nickel and Methylmagnesium Bromide

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Summary The title reaction leads to substitution at the phosphorus giving methyldiphenylphosphine and dimethylphenylphosphine.

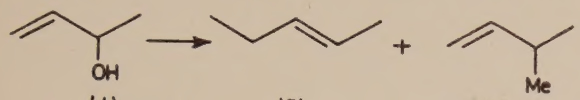
MIXTURES of phosphine–transition-metal complexes and organo-derivatives of the main-group metals are used in many catalytic reactions, and it is normally assumed that the phosphorus ligands remain unchanged. We have studied the reaction of methylmagnesium bromide with dichlorobis(triphenylphosphine)nickel (**1**) and find that reaction (1) takes place.

$$\underset{(\mathbf{1})}{(PPh_3)_2NiCl_2} \xrightarrow[\text{(ii) } H_2O]{\text{(i) MeMgBr}} PhH + PhMe + Ph_2 + \underset{(\mathbf{2})}{Ph_2MeP} + \underset{(\mathbf{3})}{PhMe_2P} \qquad (1)$$

Detectable amounts (g.c.) of benzene, toluene, and biphenyl were formed in less than 15 min when the complex (**1**) was treated at room temperature with an excess of methylmagnesium bromide in ether. After six days, the same reaction mixture afforded biphenyl†‡ [0·7 mol per mol of (**1**)], and the mixed phosphines§ (**2**) and (**3**) in a ratio of 2:1. When, after 15 h, acetone was added to the

† Identified by retention time and spectra.
‡ Biphenyl was also formed when n-propylmagnesium bromide was used instead of methylmagnesium bromide.
§ Identified by n.m.r. Trimethylphosphine, if formed, would have escaped detection.

reaction mixture before hydrolysis, dimethylphenylmethanol† was formed, and allylbenzene† was formed when allyl alcohol was added.¶ Finally, when α-methylallyl alcohol (**4**) was added to an aged (6 days) mixture of (**1**) and methylmagnesium bromide, the olefins (**5**) and (**6**) were



(4) (5) (6)

formed in a ratio of 49 : 51, the ratio being 29 : 71 with a fresh mixture.[1] Since triphenylphosphine alone does not react with methylmagnesium bromide in ether, it appears that nickel is necessary in the substitution reaction. Substitution reaction of triphenylphosphine oxide has been observed and is thought to proceed as in reaction (2).[2]

$$\underset{(\mathbf{7})}{Ph_3PO} + MeMgBr \rightarrow \underset{(\mathbf{8})}{[Ph_3MePOMgBr]} \rightarrow \underset{(\mathbf{9})}{Ph_2MePO} + PhMgBr \qquad (2)$$

The nickel atom in (**1**), like the oxygen atom in (**7**), may therefore be promoting the formation of a "phosphorane" intermediate such as (**10**), decomposition of which would lead to the methyldiphenylphosphine complex (**11**) and phenylmagnesium bromide. Substitution on phosphine ligands may thus occur more readily than has previously been suspected.[3]

$$(\mathbf{1}) \xrightarrow{MeMgBr} Ph_3P\text{–}\overset{Me}{\overset{|}{(Ni)}}\text{–} \xrightarrow{MeMgBr} \underset{(\mathbf{10})}{[Ph_3MeP\text{–}\overset{Me}{\overset{|}{(Ni)}}\text{–}MgBr]} \rightarrow \underset{(\mathbf{11})}{Ph_2MeP\text{–}\overset{Me}{\overset{|}{(Ni)}}\text{–}} + PhMgBr$$

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¶ Allylbenzene is formed in high yield from allyl alcohol and phenylmagnesium bromide in the presence of (**1**).[1]

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[2] D. Seyferth, D. E. Welch, and J. K. Heeren, *J. Amer. Chem. Soc.*, 1964, **86**, 1100.
[3] Cleavage of a phenyl group from a triphenylphosphine ligand has been recently reported: D. R. Coulson, *Chem. Comm.*, 1968, 1530; G. Speier and L. Marko, *J. Organometallic Chem.*, 1970, **21**, P46.